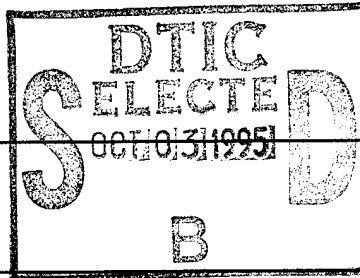


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13. ABSTRACT (Maximum 200 words) The surface chemistry and topography of carbon fiber surfaces have been probed using a variety of surface analytical tools in order to understand the processes that effect the oxidation of carbon-carbon composites. Core and Valence Band X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and other techniques were used to monitor the surface chemistry and topography of carbon fibers, with and without oxidation protective coatings. A special high vacuum apparatus was built to study surface oxidation at elevated temperatures in a chamber directly attached to a surface spectrometer. The valence band XPS spectra were interpreted by calculations that modelled the fiber surface and interfacial chemistry. The results of the project provide a better understanding of the interfacial chemistry associated with carbon fiber surface oxidation and protection. Protective films for the outer surface of the composite, and coupling agents that improve the oxidation resistance of the carbon fiber-carbon matrix interface are reported.					
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Final Report
for
Grant F49620-92-J-0144

Peter M.A. Sherwood, Principal Investigator
Department of Chemistry, Kansas State University

Contents

1. Objectives.....	1
2. Status of Effort.....	1
3. Accomplishments/New Findings.....	1
(i) Analytical Probes.....	1
(ii) Construction and Operation of a Special High Vacuum Apparatus.....	2
(iii) Reporting Accurate XPS Data for Carbon and Carbon Fibers.....	2
(iv) The Investigation of Potentially Oxidation Protective Films.....	2
(v) Monitoring Restance to Oxidizing Environments.....	2
(vi) Involvement of Carbon Composite Preparations by Enhancement of Interfacial Chemical Interactions.....	2
(vii) Building up a "mini" Carbon-Carbon Composite.....	3
(viii) Calculations.....	3
4. Personnel Supported.....	3
5. Publications.....	4
6. Interactions/Transitions.....	6
7. New discoveries, inventions, or patent disclosures.....	8
8. Honors/Awards.....	8

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Objectives

Grant F49620-92-J-0144 was awarded to support a project that used a novel combination of core and valence band X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD) and other techniques to monitor the surface chemistry associated with carbon-carbon composites and their oxidation protection. The approach is aimed at developing an understanding from which better oxidation protection approaches can be developed.

Status of Effort

The project has achieved the goals set in the original proposal, with details given in the next section. A special apparatus for treating carbon fibers with protective coatings and for producing "mini" carbon-carbon composites has been developed and used. Surface chemical information has been obtained from various surface analytical tools, especially core and valence band photoemission. These studies have allowed the interfacial chemistry to be identified, and this interfacial chemistry related to the oxidation behavior. X-alpha and *ab initio* calculations, performed on IBM RISC/6000 workstations, allowed the valence band XPS region to be interpreted, and greatly assisted its use in detecting subtle differences in surface film composition and in investigating interface chemistry. The work has shown how important chemical considerations are when the question of carbon-carbon oxidation protection is considered.

Accomplishments/New Findings

All the papers listed below have been submitted to AFOSR, thus detailed information about this work is readily accessible in published form. The description below provides a summary of this work which relates these studies to the overall goals of the project.

Progress under the grant

Most of the goals of the initial proposal have been achieved. So far, twenty four papers have been published¹⁻²⁴, and two papers are in preparation.^{25,26} The most notable accomplishments on the planned program of study were in the following areas:

Analytical Probes: The range of analytical probes of surface chemistry and topography has been extended from that originally envisaged. Core and valence band XPS, XRD and scanning electron microscopy (SEM) has been used as originally planned. In the second year of the project the principal investigator (PI) placed an electron microprobe into operation. This apparatus serves as an SEM, but also has both energy dispersive and wavelength dispersive X-ray capabilities. An important feature of this equipment is the ability to map even light elements (C,O,and N) with high intensity by using a new state-of-the-art synthetic crystal in the monochromator for X-radiation from light elements. We have shown that this allows elemental mapping of the surface of carbon fibers, with and without potentially protective films on them.^{15,17} Recently (since January 1994) the PI has had the use of an AFM and STM apparatus, purchased with funds from ARO for Professor

Klabunde's research. This has allowed us to obtain effective AFM pictures of carbon fibers with and without protective films on them, showing significant topographical changes.²¹

Construction and Operation of a Special High Vacuum Apparatus: The grant provided equipment for the construction of a high vacuum apparatus, attached to one of our XPS instruments, that allows carbon fibers to be coated with protective films and organic materials for carbonization to make a "mini" carbon-carbon composite.¹⁵ The chamber allows a sample to be treated in various gas atmospheres or at different vacuum levels in the chamber. Carbon fiber samples can be heated to over 2000°C by passing up to 20A of dc current through the fiber, and the temperature of the fiber can be monitored by an optical pyrometer mounted just outside the viewport of the chamber. The gas phase in the chamber can be analyzed by a quadrupole mass spectrometer. The sample can also be bombarded with an ion gun.

Reporting Accurate XPS Data for Carbon and Carbon Fibers: Thirteen papers²⁻¹⁴ have been published in *Surface Science Spectra* that report accurate XPS data for carbon and carbon fibers.

The Investigation of Potentially Oxidation Protective Films: Five types of potentially protective films have been investigated to date. Oxidized magnesium and aluminum films have been prepared on carbon fiber surfaces in the special apparatus discussed above.¹⁵ These films have been shown to adhere to the fiber surfaces even at high temperatures (1300°C). The three other types of film studied have been prepared externally by chemical vapor deposition (CVD) using an apparatus in the KSU chemical engineering department. Films of Si₃N₄ have been found to be susceptible to cracking, as a result of heating, from argon ion and oxygen ion etching, and by sample biasing.¹⁷ Films of SiC and SiO₂ appear to be less susceptible to cracking.²¹ We have examined the preparation of aluminum nitride films by nitrogen ion implantation²³ and hope to be able to develop aluminum nitride protective films on carbon fibers in future studies. We are currently examining a new boron-silicon-nitrogen material that has been developed by Bayer. This work is being carried out with the support of Bayer, and they have provided us with the necessary material to treat fiber surfaces. A special apparatus has been developed to coat the fibers, and we have successfully coated a number of fiber surfaces, and performed surface analysis on these films. We hope to publish this study soon, and a preliminary report of this work has been submitted to AFOSR.

Monitoring Resistance to Oxidizing Environments: Oxygen ion etching has been used as an oxidizing environment to investigate the effect of oxidation on fibers coated with potentially protective films. The extent to which a particular coating can cause enhanced oxidation resistance has been examined by investigation of the mass loss resulting from heating in air using thermal gravimetric analysis (TGA).^{16,20} The extent to which this method is effective has also been monitored by taking into account effects such as oxidative attack along the fiber axis, and through cracks in the protective films.

Improvement of Carbon Composite Preparations by Enhancement of Interfacial Chemical Interactions: We have investigated methods for enhancing the interaction of carbon fibers with the resin precursor. The effect that surface treatment has on the fibers has been monitored^{16,20} and it has been found that prior fiber surface treatment leads to better oxidation resistance of the resulting carbon-carbon composites. Interfacial chemical reactions between the treated fiber and precursor resins (phenolic resins) have been examined, and the chemical interaction enhanced by using coupling agents that react with both the surface treated fiber and the phenolic resins. The interface chemistry has been monitored by core and valence band XPS using a thin film technique.^{16,20} We have found titanium alkoxide to be a very effective coupling agent that can lead to a substantial

improvement in oxidation protection.²² We found an unusually high affinity of oxidized surfaces for sodium ions during these studies.²⁴

Building up a "mini" Carbon-Carbon Composite: We have been able to prepare a "mini" carbon-carbon composite on magnesium oxide and aluminum oxide protected fibers. This was achieved by coating the magnesium or aluminum oxide covered fibers (prepared in the special apparatus described above) with a phenolic resin (whose thickness was controlled by dipping the fibers into a solution of resin), and then carbonizing the coated fibers by electrical heating in the special apparatus in the presence of an inert atmosphere. These experiments have shown that it is possible to get a uniform coverage of carbon over the coated fibers, and illustrate how this approach provides a "step-by-step" probe of the carbon-carbon composite preparation process.²⁵

Calculations: Many calculations have been performed in order to interpret the core and valence band spectra of resin precursors and the interface between these resin precursors and surface treated carbon fibers.^{16,20} The calculations have shown how core and valence band photoemission can reasonably detect changes in the chemistry at this interface region, allowing cases where chemical interaction has occurred to be identified. Most calculations have been carried out using *ab initio* Hartree-Fock calculations, which we have used successfully in the study of other polymer systems. Valence band photoemission has been found by us and others to be especially valuable in this area.

Personnel Supported

The grant has supported a number of graduate students and postdoctoral fellows.

Faculty

Professor Peter M.A. Sherwood

Ph.D. Students supported

Tiejun Wang (Ph.D.) 1995 (Jan)

Michael Rooke (Ph.D. expected in May 1996)

Nathan Havercroft (1st year Ph.D. student)

Hema Viswanathan (1st year Ph.D. student)

Postdoctoral fellows supported

Dr. Yaoming Xie (1992-1994)

Dr. Cara Weitzsacker (1994)

Publications

Publications acknowledging support from F496620-92-J-0144

- 1 P.M.A. Sherwood, "Surface Chemical Modification and Analysis of Carbon Fibers - The Key to Novel Composites", *Materials Research Society Proceedings*, **270**, 79-89, 1992.
- 2 Y. Xie and P.M.A. Sherwood, "P-55X Pitch-based Carbon Fiber by Core Level and Valence Band XPS", *Surface Science Spectra*, **2**, 192-197, 1992.
- 3 Y. Xie and P.M.A. Sherwood, "E-35 Pitch-based Carbon Fiber by Core Level and Valence Band XPS", *Surface Science Spectra*, **2**, 198-203, 1992.
- 4 Y. Xie and P.M.A. Sherwood, "E-75 Pitch-based Carbon Fiber by Core Level and Valence Band XPS", *Surface Science Spectra*, **2**, 204-209, 1992.
- 5 Y. Xie, T. Wang, M.A. Rooke and P.M.A. Sherwood, "E-120 Pitch-based Carbon Fiber by Core Level and Valence Band XPS", *Surface Science Spectra*, **2**, 210-215, 1992.
- 6 Y. Xie and P.M.A. Sherwood, "Type II PAN-based Carbon Fiber by Core Level and Valence Band XPS", *Surface Science Spectra*, **2**, 216-221, 1992.
- 7 Y. Xie and P.M.A. Sherwood, "AU4 PAN-based Carbon Fiber by Core Level and Valence Band XPS", *Surface Science Spectra*, **2**, 222-227, 1992.
- 8 Y. Xie, T. Wang and P.M.A. Sherwood, "Core Level and Valence Band XPS Spectra of E-120 Pitch-based Carbon Fiber Potentiostatically Oxidized in Ammonium Carbonate Solution", *Surface Science Spectra*, **3**, 247-253, 1992 (published 1993).
- 9 Y. Xie and P.M.A. Sherwood, "Highly oriented pyrolytic graphite by Core Level and Valence Band XPS", *Surface Science Spectra*, **3**, 253-258, 1992 (published 1993).
- 10 Y. Xie and P.M.A. Sherwood, "Core Level and Valence Band XPS Spectra of E-120 Pitch-based Carbon Fiber Potentiostatically Oxidized in Nitric Acid Solution", *Surface Science Spectra*, **3**, 259-264, 1992 (published 1993).
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- 13 Y. Xie and P.M.A. Sherwood, "AS4 PAN-based Carbon Fiber by Core Level and Valence Band XPS", *Surface Science Spectra*, **3**, 306-311, 1992 (published 1993).
- 14 Y. Xie and P.M.A. Sherwood, "Core level and valence band spectra of an ultra high purity graphite electrode", *Surface Science Spectra*, **4**, 367-372, 1992 (published 1993).
- 15 Y. Xie and P.M.A. Sherwood, "Studies of coatings of aluminum oxide and magnesium oxide on carbon", *Chemistry of Materials*, **6**, 650-657, 1994.
- 16 T. Wang and P.M.A. Sherwood, "X-Ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces. Part XVII: Interfacial Interactions between Phenolic Resin and Carbon Fibers Electrochemically Oxidized in Nitric Acid and Phosphoric Acid Solutions, and their effect on Oxidation Behavior", *Chemistry of Materials*, **6**, 788-795, 1994.

- 17 M.A. Rooke and P.M.A. Sherwood, "X-ray Photoelectron Spectroscopic Study of Ion Etching and Electrical Biasing of Silicon Nitride on a Carbon Fiber", *Surface and Interface Analysis*, **21**, 681-690, 1994.
- 18 P.M.A. Sherwood, "The Surface Chemistry of Carbon Fibers and its Importance in Composite Behavior", in "Carbon Technology", Proceedings of Ninth Annual Conference on Materials Technology - October 26,27, 1993", Materials Technology Center, Southern Illinois University at Carbondale, 123-142, 1994.
- 19 P.M.A. Sherwood, "Surface Analysis of Carbon and Carbon Fibers for Composites", invited review article, *J. Electron Spectroscopy and Related Phenomena*, accepted for publication.
- 20 T. Wang and P.M.A. Sherwood, "X-ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces. Part 18: Interfacial Interactions between Phenolic Resin and Carbon Fiber Electrochemically Oxidized in Ammonium Carbonate Solution and Their Effect on Oxidation Behavior", *Chem. Mater.* **7**, 1020-1030, 1995.
- 21 M.A. Rooke and P.M.A. Sherwood, "X-ray Photoelectron Spectroscopic Study of Silicon Carbide films on Carbon Fibers", *Carbon*, **33**, 375-380, 1995.
- 22 T. Wang and P.M.A. Sherwood, "X-ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces. Part 20: Interfacial Interactions between Phenolic Resin and Electrochemically Oxidized Carbon Fiber Using Titanium Alkoxide Coupling Agents and Their Effect on Oxidation Behavior", *Chem. Mater.* **7**, 1031-1040, 1995.
- 23 M.A. Rooke, John A. Rotole and P.M.A. Sherwood, "An x-ray photoelectron spectroscopic study of voltage bias implantation and nitrogen etching of aluminum, *J. Vac. Sci. Technol.* , **A13**, 1299-1303, 1995.
- 24 T. Wang and P.M.A. Sherwood, "Surface Studies of the Enhanced Adsorption of Sodium Ions onto Oxidized Surfaces in Acetone-containing Aqueous Solutions", *Surf. Interface Anal.*, **23**, 659-664, 1995.
- 25 Y.Xie, C.L. Weitzsacker and P.M.A. Sherwood, "X-ray Photoelectron Spectroscopic Studies of Carbon Fiber Surfaces. Part XXI: The preparation of a carbon-carbon composite of protected carbon fibers", in preparation.
- 26 M.A. Rooke and P.M.A. Sherwood, "Surface Studies of Oxidation Protective Films involving B/Si/N compounds on Carbon Fiber Surfaces", in preparation.

Interactions/Transactions

a) Participation/presentations at meetings, conferences, seminars, etc.

The work discussed at these meetings has in most cases been either solely or partly concerned with this project.

- March 27th 1992 Department of Chemistry, University of Illinois, Urbana-Champaign. Invited Seminar
- April 17th 1992 Department of Chemistry, University of Southern Illinois at Carbondale. Invited Seminar
- April 24th 1992 Department of Chemistry, University of California, Irvine
Invited Seminar
- April 28th 1992 Materials Research Society, Spring Meeting, San Francisco
Novel Forms of Carbon, Invited Speaker
- May 25th 1992 American Carbon Society, Atlanta Meeting.
Invited Speaker
- September 3rd 1992 Department of Chemistry, Analytical Institute,
University of Bari, Italy. Invited Seminar
- September 4th 1992 Department of Chemistry, Analytical Institute,
University of Bari, Italy. Invited Seminar
- September 9th 1992 12th International Symposium on Microchemical Techniques
Cordoba, Spain
Keynote Lecture
- September 21st 1992 Seventh Annual Air Force Workshop, "Surface Reactions
in the Space Environment" - North Shore Hilton, Skokie,
Illinois. Invited Speaker
- October 27th 1992 Air Force Contractors Meeting, Washington D.C.
(Molecular Dynamics Meeting) Invited Poster
- November 11th 1992 American Vacuum Society, National Symposium
Chicago, Illinois. Oral Contributed Paper
- November 16th 1992 Department of Chemistry, Emporia State University
Invited Speaker
- Feb. 10th 1993 Department of Chemistry, Wichita State University
Invited Seminar
- Feb. 22nd 1993 NASA Langley Research Center. Presentations made by self
and Dr. Weitzacker, and M. Bellamy.
- March 31st 1993 American Chemical Society, National Meeting, Denver
30 minute talk. Members of the group made two other
oral presentations, and four poster presentations.
- April 23rd 1993 Materials Research Center, University of Pittsburgh
Invited Seminar

June 29th 1993 Wright Patterson Air Force Base, AFOSR Materials Meeting
Invited Seminar

Oct 18th 1993 Air Force Contractors Meeting, Irvine California
Invited Seminar

Oct 26th 1993 Materials Research Center, Southern Illinois University
Invited Seminar at Carbon Conference

Nov 17th 1993 American Vacuum Society, National Meeting Oral
presentation made by Dr. Cara Weitzsacker (postdoc with
group)

May 20th 1994 Raychem Research Laboratories, Palo Alto, California
Invited Seminar

May 23rd 1994 Electrochemical Society, National Meeting, San
Francisco, CA, May 22-27 1994
"Valence Band Photoemission as an Effective Probe of
Material Interactions" - Invited Seminar

May 26th 1994 Electrochemical Society, National Meeting, San
Francisco, CA, May 22-27 1994
"Corrosion and Oxidation of Nickel and Molybdenum Systems
Studied by Core and Valence Band Photoemission using an
anaerobic electrochemical cell" - Invited Seminar

September 14th 1994 AFOSR/URI C/C Composites Conference at Pennsylvania
State University.
"Interfacial Chemistry and Oxidation Protection of
Carbon Fibers for Carbon/Carbon Composites"

September 21st 1994 Department Seminar, Wichita State University

October 2nd 1994 FACCS Meeting St. Louis
Invited Seminar on Industrial Funding during meeting of
past and present federal Program Officers

October 26th 1994 American Vacuum Society Meeting, Denver
Contributed Paper presented as poster.

November 15th 1994 Invited Seminar - Alcoa, Pittsburgh, PA

May 1995 Moderator for Data Processing Session " AES: From Physics to Data"
French Vacuum Society, near Grenoble, France

July 17 1995 NASA Langley "Presentation on Studies of Carbon Fiber Surfaces"

August 24th 1995 American Chemical Society National Meeting. Invited Paper

*b). Consultative and advisory functions to other laboratories and
agencies*

See AFOSR and Air Force Meetings in list above.

c) Transitions

Discussions with industry have included Dupont, Amoco, Alcoa, Raychem. These discussions often included discussion of work funded by this project.

New Discoveries, inventions, or patent disclosures

The conclusion of many of the published studies promise to be important in the development of new oxidation protection approaches for carbon-carbon composites.

Honors/Awards

During Grant Period

Sc.D. Degree from the University of Cambridge in England (1995). This degree is awarded after submission of a complete set of publications for evaluation of "distinction by some original contribution to the advancement of science or of learning".

Prior to Grant Period

Fellow of the Royal Society of Chemistry (1982)

Salters Company Fellow (1970-1972)

Forrester Prize and Irvine Jubilee Medal (1967) (Best first class honors degree in Chemistry, St. Andrews University, Scotland)

Finlayson Prize and W.J. Matheson Bursar (1965)